



Influence of NO_x and Air on the Ageing Behaviour of MoDTC

A. Ponjavic¹ · T. Lemaigre¹ · M. Southby² · H. A. Spikes¹ 

Received: 17 January 2017 / Accepted: 14 March 2017
© The Author(s) 2017. This article is an open access publication

Abstract Molybdenum dialkyldithiocarbamates (MoDTCs) are very effective friction modifier additives for use in engine oils and other lubricants. However, as engine oils age during extended drain intervals, MoDTCs can lose some or all of their ability to reduce friction and this is generally believed to result from their oxidative degradation. In this study, MoDTC solutions in base oil have been subjected to oil ageing in a controlled NO_x/air flow rate, controlled temperature test apparatus and the effect of ageing on the ability of the MoDTC to reduce friction has been explored. As shown in previous studies, the additive's friction-reducing properties are completely lost after a quite short period of ageing at 160 °C. However, it was found that at this temperature the presence of NO_x has little if any influence on the rate of friction loss, indicating that the latter is controlled primarily by the rate of reaction of oxygen with the base oil and thus the rate of consumption of MoDTC as a peroxide decomposer. By contrast, when ageing tests are carried out at lower temperatures it is found that NO_x has a very strong effect on the rate at which MoDTC loses its ability to reduce friction, so that at 100 °C NO_x accelerates this rate by two orders of magnitude compared to air alone. This suggests that at low temperatures the rate at which MoDTC is consumed is controlled by its reaction as a radical inhibitor with NO_x species.

Keywords Friction modifier · MoDTC · Lubricant degradation · Boundary friction · MoS₂

1 Background

As engine oil viscosities are progressively lowered in order to reduce hydrodynamic friction, so the use of friction modifier additives to reduce friction in the mixed lubrication regime becomes increasingly important. There are several different classes of friction modifier additives [1], but one of the most effective is the family of soluble organomolybdenum additives and in particular the molybdenum dialkyldithiocarbamates (MoDTCs). Under optimal conditions these are able to reduce friction coefficient down to values of around 0.04–0.06. MoDTCs reduce friction by reacting with rubbing surfaces to form low-shear strength 2D nanocrystals of MoS₂. This can occur on both steel surfaces [2] and also on the phosphorus-based films formed by the antiwear additive zinc dialkyldithiophosphate [3]. Since this reaction appears to occur only at the asperity tips where rubbing solid–solid contact occurs, it has a disproportionate effect in reducing boundary friction [2].

It has been shown that MoDTCs are only effective in reducing friction above a critical temperature and a critical concentration, although the values of both of these thresholds depend on the MoDTC type [4]. For dimeric MoDTCs, a concentration of at least 150 ppm Mo and a bulk temperature of 50 °C are generally required to reduce friction [4], but for trimeric MoDTCs, concentrations of less than 100 ppm are effective [5]. The reason for the temperature threshold of activity is not yet known, but trimers are suggested to be more reactive, and thus work at lower concentrations, because of their molybdenum atoms having the same valence state as that present in their low-friction product MoS₂ [6].

The principle limitation of organomolybdenum friction modifier additives in engine oils is generally recognised to

✉ H. A. Spikes
h.spikes@imperial.ac.uk

¹ Tribology Group, Imperial College, London, UK

² Lubricants Discovery Hub, Shell Global Solutions, Manchester, UK

be that they can lose of their ability to reduce friction as the oil ages during engine operation. This may occur within the normal drain interval of engine oils and was an important contributor to the inclusion of measurement of fuel efficiency retention within the gasoline engine oil specification ILSAC GF3 in 2000, a requirement that has continued in subsequent engine oil specifications.

The influence of oil ageing on the longevity of MoDTC and thus on its friction-reducing properties was investigated using both engine tests and bench oxidation tests throughout the 1990s. In 1990, Igarashi et al. [7] used a combination of a bench oxidation and a friction test to show that MoDTC lost its ability to reduce friction during oxidative degradation of the lubricant and that this loss was accompanied by a progressive lowering of MoDTC concentration in solution from its original value. Igarashi suggested that the deterioration of friction properties of oils containing MoDTC could be due both to the loss of MoDTC by oxidative degradation and to accumulation of oil oxidation products that block MoS_2 formation on rubbed surfaces.

In 1995, both Arai et al. [8] and Jensen et al. [9] applied bench oxidation tests in which a mixture of air and NO_x was bubbled through heated oil to study MoDTC performance. Nitrogen oxides (NO_x) are produced in crankcase engines during high-temperature combustion and are both free radicals and potential oxygen donors. They are thus likely to be implicated in oxidative degradation and so should be present when mimicking the chemical environment around the engine piston zone. Again, the ability of MoDTC to reduce friction was lost during oil oxidation and this correlated with loss of MoDTC from solution. Both studies also showed a good match in terms of oil degradation and friction loss between their bench oxidation tests and engine tests and both concluded that the principle reason for MoDTC's loss of friction-reducing performance was oxidative degradation of the additive in solution.

Graham et al. [10] combined an air/ NO_x -based oil oxidation test, reverse-phase high-pressure liquid chromatography (HPLC) and HFRR friction measurements to study the influence of oil ageing on MoDTC degradation. They found that the rate of MoDTC loss as measured by HPLC and the oxidation time needed to lose friction-reducing capability both varied depending on the MoDTC structure and purity. However, the two behaviours were always correlated, so that friction-reducing ability was always lost when the MoDTC concentration fell below a critical value.

Several researchers have studied the impact of other additives on MoDTC's loss of friction-reducing ability during ageing. One important interaction of MoDTC is with zinc dialkyldithiophosphate (ZDDP) which is always present in engine oils. Korcek et al. identified a ligand exchange reaction in solution that partially converted $\text{ZDDP} + \text{MoDTC}$ to $\text{MoDDP} + \text{ZDTC}$ and lowered the

initial concentration of MoDTC [11–14]. However, Graham showed that the addition of ZDDP to MoDTC reduced the rate at which MoDTC was lost during degradation and also delayed the latter's loss of friction-reducing ability [9]. Korcek suggested that since ZDDP was a stronger peroxide decomposer and ZDTC a stronger radical inhibitor than the corresponding Mo compounds the ZDDP acted and was consumed as an antioxidant in preference to MoDTC, thereby extending the latter's useful life [13]. MoDTC then only lost its friction-reducing effectiveness when all the ZDDP was used up. Research also showed that radical inhibitor-type antioxidants and sulphur-containing peroxide decomposer antioxidants could slow the rate at which MoDTC is lost while other engine oil additives and also base oil type could influence durability of the friction-reducing properties of MoDTC [7, 8, 10, 11].

Few workers have studied the how ageing alters MoDTC at a molecular level, thereby resulting in its loss of friction-reducing ability. Kubo combined gel permeation chromatography (GPC) and mass spectrometry (MS) analysis of MoDTC solutions and identified dialkyldithiocarbamic acid in aged oils, suggesting cleavage of MoDTC at the carbamate S and Mo bond [15]. Recently, based on FTIR, HPLC and MS analysis of degraded oil, Feo et al. [16] have suggested a degradation process involving S/O exchange followed by loss of S from the MoDTC and eventually scission of the dicarbamate from the Mo core.

Some work has also examined the impact of oil ageing on the surface films formed by MoDTC. It was shown using XPS and HRTEM that as the concentration of MoDTC decreases in the lubricant due to oxidative ageing, the MoS_2 sheets are modified, becoming smaller and fewer in number and possibly partially oxidised [17, 18].

The key conclusion from most of the above work is that MoDTC acts as an antioxidant and is consumed during oil oxidation in this role, so that eventually there is insufficient concentration remaining to form a low-friction film. However, it is not clear how significant is the role of NO_x in this process and thus whether MoDTC loss is likely to be specifically a problem in engine oils. Although many studies have used air/ NO_x mixture and shown in ageing tests that this depletes MoDTC and results in it losing the ability to reduce friction, similar effects have been seen when only air is present during oxidation [7, 18]. This study aims to explore the effect of NO_x on the ability of MoDTC to reduce friction.

2 Methods and Materials

A bench test oil ageing method was developed based on the Ford oil ageing batch reactor test described in [16] and used to investigate MoDTC ageing in [9]. This consists of a

multi-necked round-bottomed flask supported in a temperature-controlled magnetic stirrer heating mantle (Fig. 1). Air and a blend of 1000 ppm NO_x in air are supplied separately from cylinders via a pair of (programmable) flow controllers to enable any NO_x composition in air up to 1000 ppm to be obtained. The test conditions used in this study are listed in Table 1. 5 ml oil samples were withdrawn every 30 min during oil ageing and friction was measured in a high-frequency reciprocating rig (HFRR, PCS Instruments, Acton, UK). All HFRR tests were conducted at 1 mm stroke length, 20 Hz stroke frequency, 4 N load and a temperature of 120 °C. HFRR test duration was 20 min and friction coefficient was averaged over this time to obtain mean values for a test. AISI 52,100 steel balls and discs were employed with hardness 810 Hv (Vickers hardness) and 880 Hv, respectively. Friction values obtained from the 20 min HFRR tests were averaged and plotted as a function of ageing time.

The test oil was a commercial MoDTC dissolved at 0.3 wt%, corresponding to 135 ppm Mo, in group II base oil. The base oil viscosity was 20.1 mPas at 40 °C and 4.09 mPas at 100 °C with a viscosity index of 102. A relatively low MoDTC concentration was chosen in order to limit ageing time at the lower test temperatures.

Tests were carried out both with and without a reflux condenser in the exhaust neck to investigate whether retention of water or other low boiling components in the flask was significant. However, no significant differences were observed to result from the presence of this condenser.

Any NO_x present in the exhaust products was scavenged by passing the gas through two bottles filled with 10 wt% sodium hydroxide and 3.5 wt% hydrogen peroxide.

3 Results

Figure 2 compares HFRR friction traces for the base oil, the fresh MoDTC solution and the MoDTC solution aged for 0.5 h and for 1 h in a 770 ppm NO_x air flow at 160 °C. The fresh MoDTC solution gives an almost immediate friction reduction from the base oil value of 0.15 down to 0.08. The sample aged for 0.5 h shows an immediate

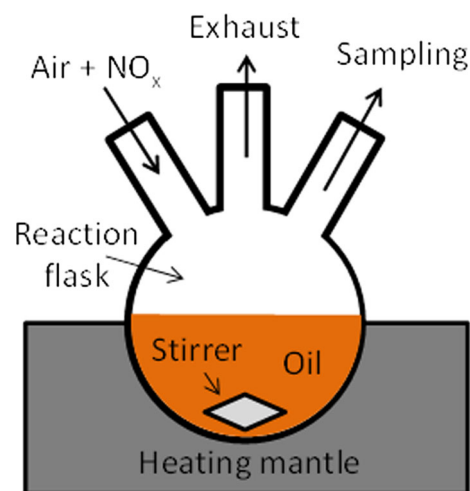


Fig. 1 Schematic diagram of oil ageing apparatus

friction reduction but this is lost over the 20 min HFRR test period. The sample aged for 1 h shows negligible friction reduction, indicating that the MoDTC has lost all of its effectiveness over this ageing period.

To confirm that the loss of MoDTC effectiveness is due to the NO_x /air flow and not simply thermal degradation, a similar test was carried out at 160 °C using a flow of argon gas at the same test temperature. As shown in Fig. 3, this gave no loss of friction-reducing ability even after 3.5 h ageing. A measurement after 10 h ageing also showed no loss of friction-reducing response.

Figure 4 shows the influence of ageing temperature on MoDTC friction-reducing capability for tests in NO_x -free air. It can be seen that the useful MoDTC life is strongly dependent on temperature, extending from 0.5 h at 160 °C to 2 h at 150 °C and 7.5 h at 140 °C. For similar tests using 770 ppm NO_x in air, the useful life was considerably shorter at 140 °C but not at 160 °C.

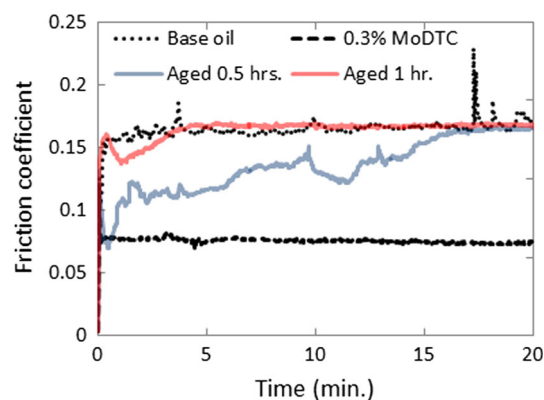


Fig. 2 Comparison of HFRR friction traces for base oil, fresh MoDTC solution, blend aged for 0.5 h and blend aged for 1 h. Ageing temperature 160 °C, 770 ppm NO_x

Table 1 Oil ageing test conditions

Initial oil volume	500 ml
Total gas flow rate	200 cm ³ /min
NO_x content of gas flow	0–770 ppm
Temperature	100–160 °C
Stir speed	350 rpm

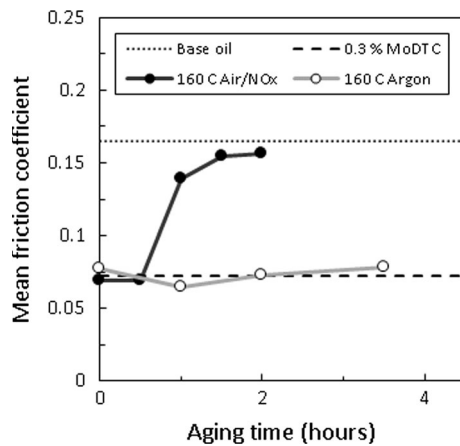


Fig. 3 Influence of argon on HFRR friction coefficient for MoDTC solution during ageing at 160 °C

To explore the relative importance of NO_x *versus* air on loss of MoDTC effectiveness, tests were carried out in which the total flow was always the same ($200 \text{ cm}^2/\text{min}$) but with three different NO_x concentrations. Figure 5 shows friction results from ageing tests at 160 °C. At this temperature, there is little difference between 100 and 770 ppm NO_x while the test with no NO_x , just $200 \text{ cm}^3/\text{min}$ air flow, appeared to give slightly faster loss of MoDTC's friction-reducing effectiveness. However, as shown in Fig. 6 a much stronger relative influence of NO_x was seen at lower ageing temperatures. This figure compares the degradation time (the ageing time by which the friction coefficient falls to half way between the base oil and fresh MoDTC solution friction coefficients) during extended ageing tests for NO_x -free air and 770 ppm NO_x gas flows at various temperatures. During ageing at 160 °C, NO_x does not significantly accelerate the loss of MoDTC effectiveness compared to air alone. However, at 100 °C

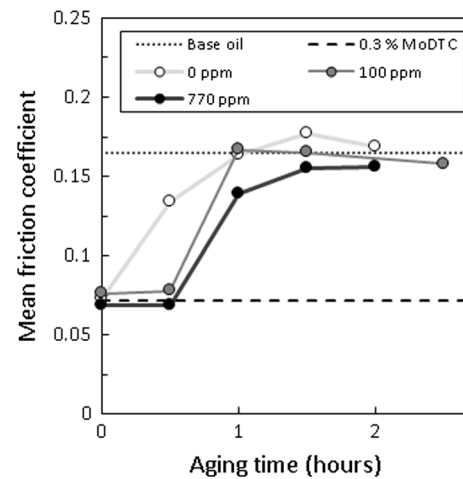


Fig. 5 Effect of NO_x concentrations during MoDTC solution ageing on HFRR friction. Ageing temperature 160 °C

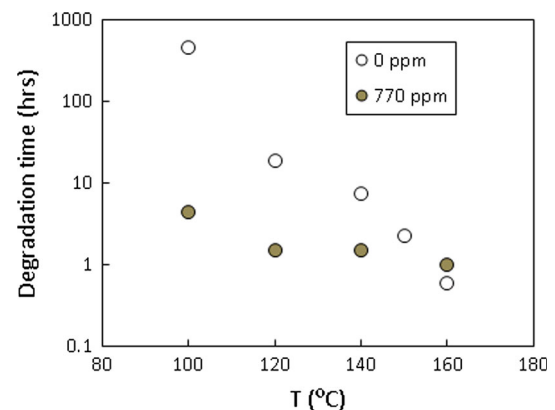


Fig. 6 Influence of temperature on the contribution of NO_x to loss of MoDTC solution friction-reducing ability

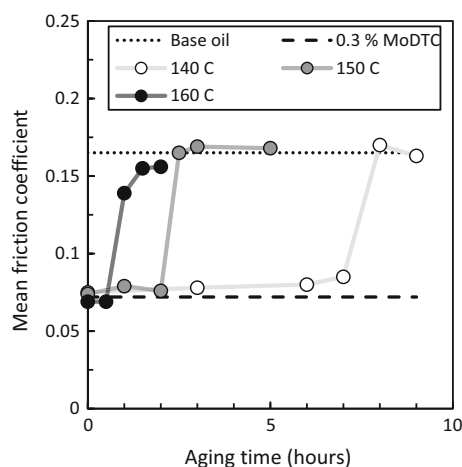


Fig. 4 Influence of ageing temperature on HFRR friction of MoDTC solutions aged with air

NO_x reduces the useful life of MoDTC by more than two orders of magnitude compared to ageing in just an air flow. Figure 7 shows how ageing time varies with NO_x concentration at the relatively low ageing temperature of 120 °C. Unlike at 160 °C, at this lower temperature the useful life of the MoDTC is strongly dependent on NO_x concentration.

4 Discussion

For the ageing tests carried out at 160 °C, the results found in this study are broadly similar to those found by other researchers, with a rapid loss of the ability of MoDTC to reduce friction during ageing. In this study, the time for this loss was shorter (0.5–1 h) compared to other work, because of the low initial MoDTC concentration. The friction traces are also somewhat different in shape from some previous work, with an initial and rapid drop of friction followed, for

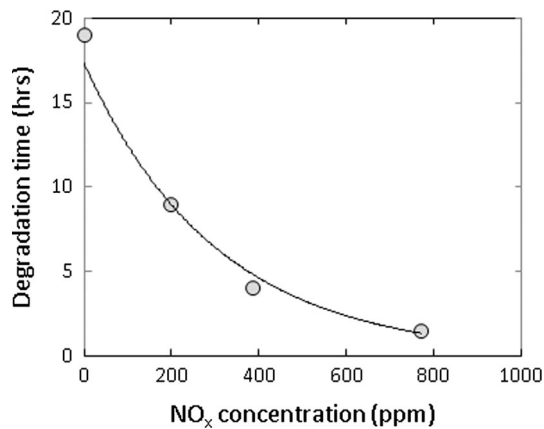


Fig. 7 Influence of NO_x concentration on the loss of MoDTC friction-reducing effectiveness at 120 °C

the partially aged samples, by a progressive rise. Some other work has seen a much slower initial friction drop followed by a rise with rubbing time.

The most important finding of the current study is that, while the presence of NO_x does not significantly accelerate the rate of loss of friction-reducing ability of MoDTC at high temperature compared to air alone, it has a very strong effect at lower temperatures. This probably reflects different responses of MoDTC to oxidation at high and low temperature. Figure 8 shows a schematic diagram of the hydrocarbon oxidation process taken from [19]. After a short induction period in which hydroperoxide is formed, an intermediary radical/peroxide chain reaction cycle consisting of reactions (4), (5), (6) and (7) is established. This can be quenched by two types of antioxidant: radical inhibitors that trap the free radicals and peroxide decomposers that convert peroxide, ROOH , to non-reactive species.

Johnson et al. [11] studied the antioxidant properties of MoDTC at two temperatures. At low temperature (60 °C), while MoDTC itself did not trap radicals it appeared to be converted during oxidation into a species with very effective radical inhibitor properties. At high temperature (160 °C), MoDTC did not act to trap free radicals but nevertheless possessed some oxidation inhibitor properties, which probably reflects a peroxide decomposing activity. Graham also showed that the addition of hydroperoxide to MoDTC oil followed by storage for 24 h at room temperature resulted in almost complete loss of both MoDTC and its friction-reducing ability, suggesting a peroxide decomposing behaviour [10].

It thus appears that during oxidative ageing at 160 °C the rate of oxidation is controlled primarily by the oxygen in the air, with NO_x having little additional effect and MoDTC acting and being consumed predominantly as a peroxide decomposer. Johnson and Korcek have discussed

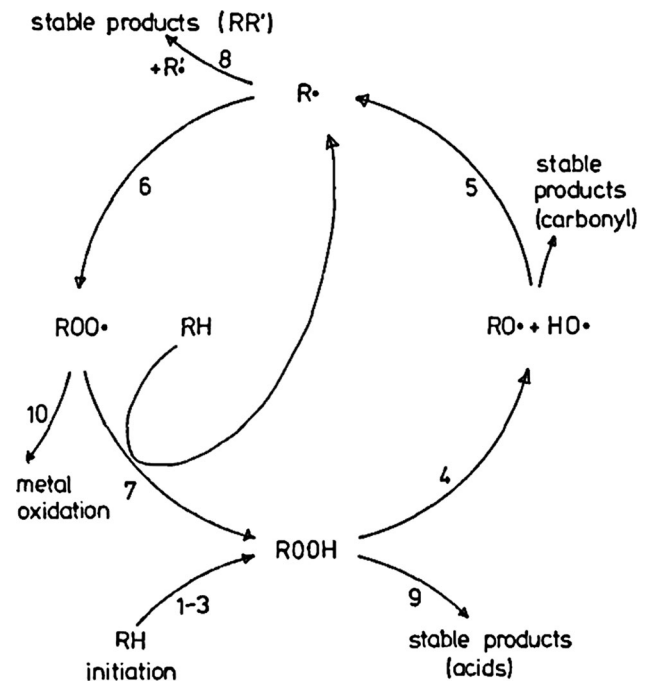


Fig. 8 Diagram to illustrate the propagation stage of hydrocarbon oxidation (from [19]). Dotted species indicate free radicals

the role of NO_x in hydrocarbon oxidation [20]. At low temperatures, the rate of oxidation is much slower, so that in the absence of NO_x MoDTC is consumed very slowly. However, NO_x components are themselves free radical species, so that now the primary reaction that consumes MoDTC is its radical inhibiting reaction with NO_x .

It is interesting to note that most previous studies of benchtop MoDTC ageing have focussed on the relatively high temperature of 160 °C. Possibly this was chosen to reflect the level of temperature present in engine ring packs, but the authors were unable to find any discussion of this choice of temperature in the literature. In a recent paper, Plumley et al. [21] have discussed the lubricant temperatures in the piston zone of crankcase engines and their impact on friction. Their study suggests that, while temperatures in the top ring zone may exceed 150 °C, they reduce rapidly down the stroke length, so that for most of the stroke length they are below 130 °C, especially when the engine does not operate under full load. Some studies have used engines to age MoDTC-containing oils and then studied the friction properties of the aged lubricant [22, 23]. This approach is extremely realistic but subjects the lubricant to a composite and poorly defined range of temperatures.

If the ageing data at three different NO_x concentrations and 120 °C shown in Fig. 7 are plotted as the reciprocal of degradation time (corresponding to ageing rate) versus NO_x ppm, a straight line is obtained, indicating that the rate of

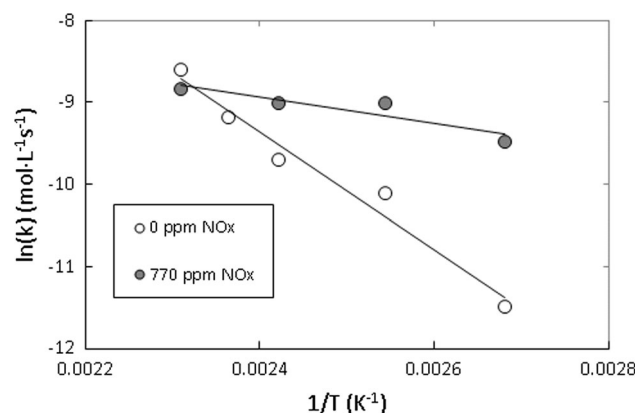


Fig. 9 Rate of loss of MoDTC friction effectiveness versus inverse temperature

MoDTC consumption at low temperatures is proportional to NO_x availability.

Figure 9 plots the logarithm of the rate of MoDTC friction reduction (simply the reciprocal of the degradation time) against the reciprocal of absolute temperature for ageing in air and NO_x /air. These give straight line plots in accord with an Arrhenius rate law with activation energies 140 kJ/mol in air and 30 kJ/mol in 700 ppm NO_x .

5 Conclusions

The influence of oil ageing on the ability of MoDTC to reduce friction in base oil solution has been studied in a controlled NO_x /air flow rate, controlled temperature test apparatus. As shown in previous studies, the additive's friction-reducing properties are completely lost after a quite short period of ageing at 160 °C. Based on previous work, this is believed to result from loss of MoDTC from solution due its consumption in the role of an oxidation inhibitor. It has been shown that at this temperature the presence of NO_x has little if any influence on the rate of friction loss, indicating that it is controlled primarily by the rate of reaction of oxygen with the base oil and thus the rate consumption of MoDTC as a peroxide decomposer.

However, when ageing tests are carried out at lower temperatures it is found that NO_x has a very strong effect on the rate at which MoDTC loses its ability to reduce friction, so that at 100 °C NO_x accelerates this rate by two orders of magnitude compared to air alone. This suggests that at low temperatures the rate at which MoDTC is consumed is controlled by its reaction as a radical inhibitor with NO_x species and is likely to be reduced to the use of appropriate inhibitors.

Acknowledgements The authors wish to thank Shell Global Solutions, UK, for supporting this research which was carried out in the

Shell University Technology Centre for Fuels and Lubricants at Imperial College London.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. Spikes, H.A.: Friction modifier additives. *Tribol. Lett.* **60**, 5 (2015)
2. Topolovec Miklozic, K., Graham, J., Spikes, H.: Chemical and physical analysis of reaction films formed by molybdenum dialkylthiocarbamate friction modifier additive using Raman and atomic force microscopy. *Tribol. Lett.* **11**, 71–81 (2001)
3. Topolovec-Miklozic, K., Forbus, T.R., Spikes, H.A.: Performance of friction modifiers on ZDDP-generated surfaces. *Tribol. Trans.* **50**, 328–335 (2007)
4. Graham, J., Korcek, S., Spikes, H.A.: The friction-reducing properties of molybdenum dialkylthiocarbamate additives. Part 1. Factors influencing friction reduction. *Tribol. Trans.* **44**, 626–636 (2001)
5. Hartley, R.J., Waddoups, M., Bell, I.A., Bidwell, T.R., Farnsworth, G.R., Miyoshi, T.: Lubricating oil composition. US Patent 6,300,291 (2001)
6. Haque, T., Morina, A., Neville, A.: Influence of friction modifier and antiwear additives on the tribological performance of a non-hydrogenated DLC coating. *Surf. Coat. Technol.* **204**, 4001–4011 (2010)
7. Igarashi, J., Yamada, Y., Ishimaru, M., Kagaya, M.: Degradation of friction modifiers. In: *Proceedings of the Japan International Tribology Conference*, Nagoya, pp. 421–426 (1990)
8. Arai, K., Yamada, M., Asano, S., Yoshizawa, S., Ohira, H., Hoshino, K., Ueda, F., Akiyama, K.: Lubricant technology to enhance the durability of low friction performance of gasoline engine oils. SAE Technical Paper No. 952533 (1995)
9. Johnson, M.D., Jensen, R.K., Clausen, E.M., Schriewer, K., Korcek, S.: Effects of aging on frictional properties of fuel efficient engine oils. SAE Technical Paper No. 952532 (1995)
10. Graham, J., Jensen, R., Spikes, H.A.: The friction-reducing properties of molybdenum dialkylthiocarbamate additives. Part 2. Durability of friction reducing capability. *Tribol. Trans.* **44**, 637–646 (2001)
11. Johnson, M., Jensen, R., Korcek, S.: Additive interactions and depletion processes in fuel efficient engine oils. SAE Technical Paper No. 971694 (1997)
12. Johnson, M.D., Jensen, R.K. and Korcek, S.: Base oil effects on friction reducing capabilities of molybdenum dialkylthiocarbamate containing engine oils. SAE Technical Paper No. 972860 (1997)
13. Korcek, S., Jensen, R.K., Johnson, M.D.: Interactions leading to formation of low friction films in systems containing molybdenum dialkylthiocarbamate and zinc dialkylthiophosphate additives. *Tribol. Ser.* **38**, 399–407 (2000)
14. Jensen, R.K., Korcek, S., Johnson, M.D.: Friction-reducing and antioxidant capabilities of engine oil additive systems under oxidative conditions. II. Understanding ligand exchange in a molybdenum dialkylthiocarbamate/zinc dialkylthiophosphate additive system in various base oils. *Lubr. Sci.* **14**(1), 25–42 (2001)

15. Kubo, K., Nagakari, M., Shitamichi, T., Motoyama, K.: The effect of ageing during engine running on the friction reduction performance of oil soluble molybdenum compounds. In: Proceedings of the International Tribology Conference, Yokohama, pp. 745–750 (1995)
16. De Feo, M., Minfray, C., Bouchet, M.D.B., Thiebaut, B., Martin, J.M.: MoDTC friction modifier additive degradation: Correlation between tribological performance and chemical changes. *RSC Advances* **5**, 93786–93796 (2015)
17. De Barros Bouchet, M., Martin, J.M., Le Mogne, T., Bilas, P., Vacher, B., Yamada, Y.: Mechanisms of MoS₂ formation by MoDTC in presence of ZnDTP: effect of oxidative degradation. *Wear* **258**, 1643–1650 (2005)
18. De Feo, M., Minfray, C., Bouchet, M.D.B., Thiebaut, B., Le Mogne, T., Vacher, B., Martin, J.M.: Ageing impact on tribological properties of MoDTC-containing base oil. *Tribol. Intern.* **92**, 126–135 (2015)
19. Newley, R.A., Spikes, H.A., Macpherson, P.B.: Oxidative wear in lubricated contact. *Trans. ASME J. Tribol.* **102**, 539–544 (1980)
20. Johnson, M.D., Korcek, S.: Effects of NO_x on liquid phase oxidation and inhibition at high temperatures. *Lubr. Sci.* **3**, 95–118 (1991)
21. Plumley, M.J., Wong, V., Molewyk, M., Park, S.-Y.: Optimizing base oil viscosity temperature dependence for power cylinder friction reduction. SAE Technical Paper No. 2014-01-1658 (2014)
22. Yoshida, S., Naitoh, Y.: The effect of ashless antioxidants type on friction reduction durability on engine oils containing MoDTC. SAE Technical Paper 2006-01-3415 (2006)
23. Yoshida, S., Naitoh, Y.: Evaluation of low phosphorus engine oil containing MoDTC. SAE Technical Paper 2007-01-1962, JSAE 20077276 (2007)